CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a group of condensed multiple benzenoid-ring chemicals formed during the incomplete combustion of coal, oil and gas, garbage, or other organic substances. Instead of carbon being completely oxidized to carbon dioxide, hydrocarbon fragments are generated which can interact with each other to yield complex polycyclic structures. PAHs can be man-made or occur naturally. There is no known use for most of these chemicals except for research purposes. A few of PAHs are used in medicines and to make dyes, plastics, and pesticide [5].

As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. Most PAHs do not occur alone in the environment (including those found at hazardous waste sites), rather they are formed as mixtures of two or more PAHs. PAHs in general have high melting points and low vapor pressures, and are virtually insoluble in water. Many PAHs are often associated with or adsorbed onto particulate matter, and a large mass fraction of airborne PAHs is associated with ultrafine particles [5]. In addition they can occur in soil or sediment as solids.

Badger, first postulated a synthetic route to PAH formation outlined in Figure 2.1 [6]. His pyrolysis studies were conducted by passing the hydrocarbon vapor in nitrogen through a silica tube at 700°C.

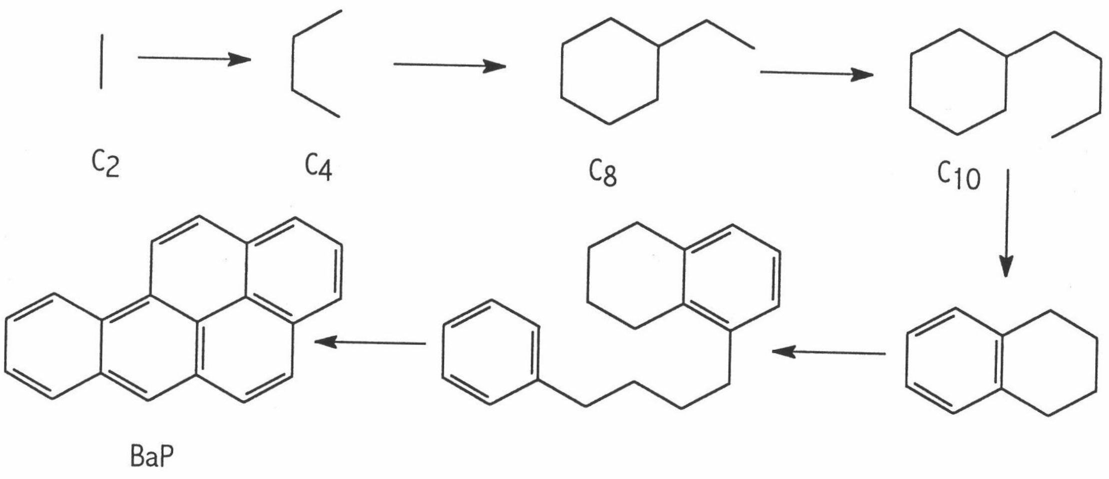


Figure 2.1 Mechanism of Benzo(*a*)pyrene Formation

Although the use of nitrogen atmosphere has been criticized as lacking relevance to actual combustion, the reducing conditions are similar to those of the oxygen-deficient environments of a flame, and the data are in good qualitative agreement with the PAH combustion products formed. For example, Boubel and Ripperton found that benzo(*a*)pyrene (BaP) is produced during combustion even at high percentages of excess air, but that the amount of BaP is greater at lower percentages of excess air (quoted in [6]).

In 1993, Williams and Taylor studied the aromatization of tyre pyrolysis oil to yield polycyclic aromatic hydrocarbons. Shredded scrap automotive tyres were pyrolysed in a static batch reactor in a stream of nitrogen. The products were passed directly to a second heated reactor, where secondary reactions of the pyrolysis vapours occurred. The condensed tyre pyrolysis oil, after secondary reaction, was analyzed for the content of PAHs. The concentration of PAHs were found to increase with increasing secondary reactions involving the aromatization of olefinic compounds.

A Diels-Alder mechanism was proposed in their investigation of secondary cracking reactions of tyre oil vapour to form PAHs. When the tyre oil was subjected to secondary cracking reactions in a post-pyrolysis reactor heated to higher temperatures the concentration of individual PAHs and total PAHs increased as the temperature was increased [7].

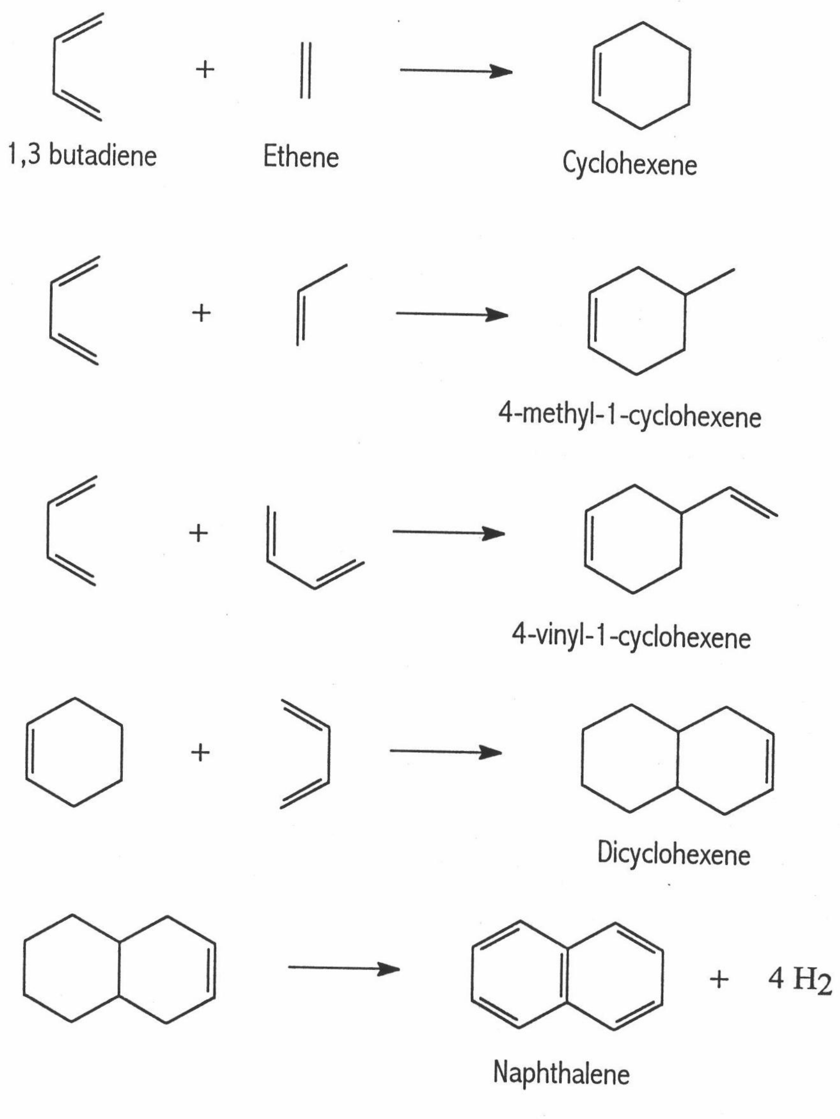


Figure 2.2 Formation of PAH in Pyrolysis Tyre Oil

2.1.1 Atmospheric Form of PAHs

Most of the PAHs are high melting/high boiling point solids that are very insoluble in water. At 25°C, the available vapor pressures of the pure compounds vary for the individual compounds from 10^{-3} kPa (3-rings) to 10^{-12} kPa (7-rings). Most PAHs are often associated with or adsorbed onto suspended particulate matter, and a large mass fraction of airborne PAHs is associated with ultrafine particles [5]. However, two- or three- ring compounds may be found partially in the vapor phase. Whether PAHs are condensed into discrete particles after cooling or are adsorbed on surfaces of existing particles is still unknown.

With the particulate form, the particle size affects the residence time of particulate matter. Urban aerosols appear to have a residence time without precipitation of 4 to 40 days for particles less than 1 μm in diameter and 0.4 to one day for particles 1 to 10 μm in diameter. Thus, the atmospheric lifetime of a PAH particle will be closely related to its particle size.

Chemical and photochemical reactivities of PAHs on particulate matter vary considerably from half-lives of less than a day to several days. Reaction rates of compounds on smaller particle sizes are likely to be faster than those of larger particles. Light irradiation considerably accelerates some reactions, but not others. However, monitoring data suggest that at least 20 PAHs are stable enough in the form found in the atmosphere that they can travel long distances with particulate matter [6].

2.1.2 Health Hazards of PAHs

The U.S. Department of Health and Human Services (DHHS) has determined that PAHs may reasonably be anticipated to be an important group of chemical carcinogens. Several of PAHs, including benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, dibenz(*a,h*)anthracene, indeno(1,2,3-*cd*)pyrene, have caused tumors in laboratory animals when they ate them, when they were applied to their skin, or when they breathed them in the air for long periods of time. Reports on humans show that individuals exposed by breathing or skin contact for long periods of time to mixtures of other compounds and PAHs can also develop cancer [2].

Studies on animals have also shown that PAHs can cause harmful effects on skin, body fluids, and the body's system for fighting disease after both short- and long-term exposure. These effects have not been reported on humans. As can be seen, no information is available from human studies to determine health effect resulting from exposure to specific levels of the individual PAHs, although inhalation and skin exposure to mixtures containing PAHs has been associated with cancer in humans.

Several investigators have studied the mechanism of carcinogenic action of a wide range of PAHs in the biological systems and animal tumor bioassay systems. The key event of chemical carcinogenesis is the covalent binding of the carcinogen to macromolecules, especially to DNA, in the cell. PAHs are large, flat compounds that are similar to benzene in structure. Many aromatic compounds, including PAHs are carcinogenic as a result of their structure. The flat hydrophobic shape of PAH makes it difficult to excrete from the body. In addition, this shape allows PAH to insert into the structure of DNA where it interferes with the proper functioning of the DNA and can lead to cancer.

In addition, during their migration through the environment, PAHs may be transformed, by interaction with oxidants and sunlight, into products which, in some cases, are much more mutagenic than the compounds from which they were derived.

Although the health effects of the individual PAHs are not exactly alike, the following 16 PAHs, classified as priority pollutants by the U.S. EPA, are considered in this study. Their chemical structures are show in Figure 2.3.

PAHs	Formula	M.W.
1. Naphthalene	$C_{10}H_8$	128
2. Acenaphthylene	$C_{12}H_8$	152
3. Acenaphthene	$C_{12}H_{10}$	154
4. Fluorene	$C_{10}H_8$	166
5. Phenanthrene	$C_{14}H_{10}$	178
6. Anthracene	$C_{14}H_{10}$	178
7. Fluoranthene	$C_{16}H_{10}$	202
8. Pyrene	$C_{16}H_{10}$	202
9. Chrysene	$C_{18}H_{12}$	228
10. Benz(*a*)anthracene	$C_{18}H_{12}$	228
11. Benzo(*b*)fluoranthene	$C_{20}H_{12}$	252
12. Benzo(*k*)fluoranthene	$C_{20}H_{12}$	252
13. Benzo(*a*)pyrene	$C_{20}H_{12}$	252
14. Indeno(1,2,3-*cd*)pyrene	$C_{22}H_{12}$	276
15. Benzo(*ghi*)perylene	$C_{22}H_{12}$	276
16. Dibenz(*a,h*)anthracene	$C_{22}H_{14}$	278

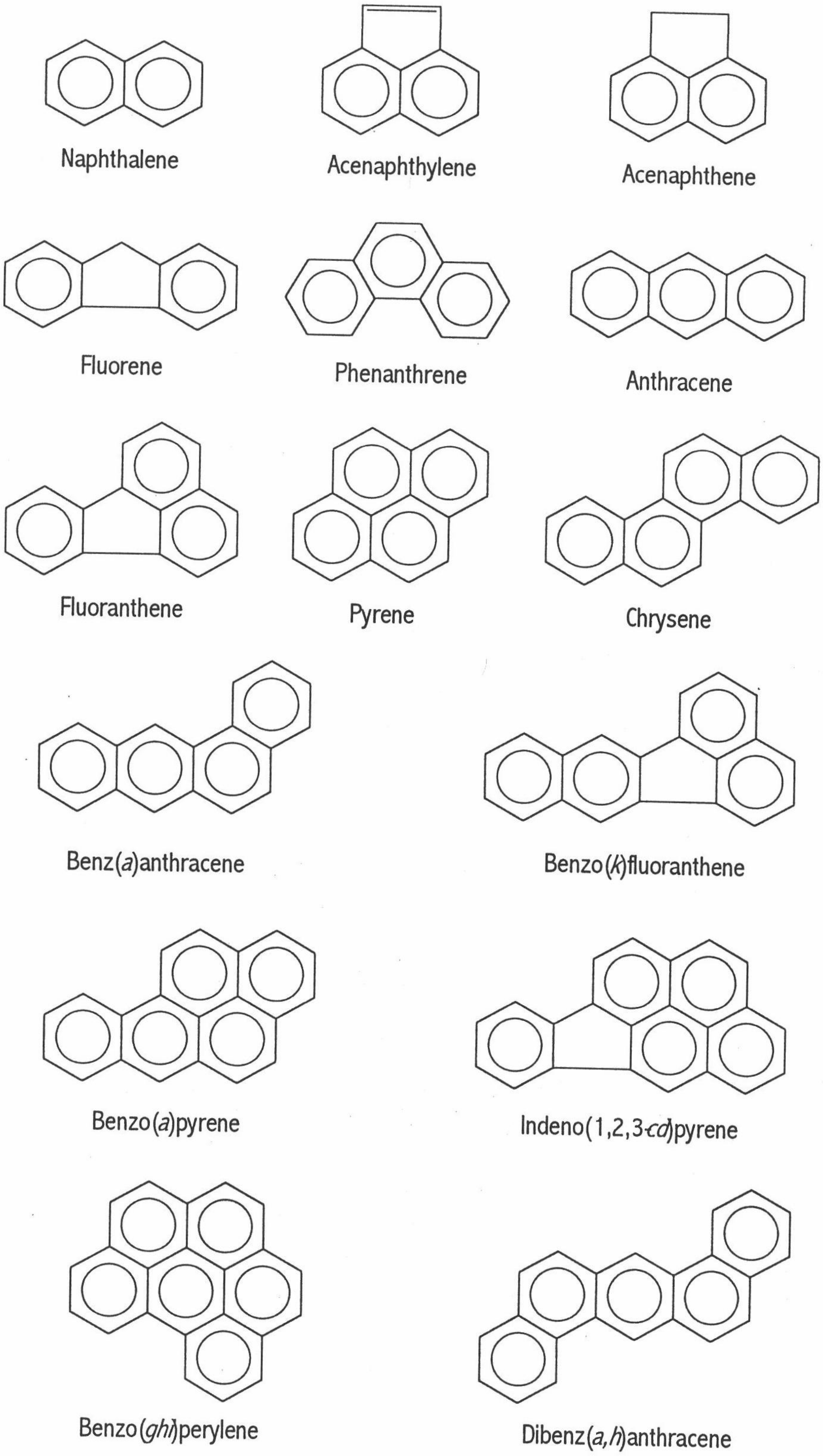

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Chrysene
Benz(*a*)anthracene
Benzo(*k*)fluoranthene
Benzo(*a*)pyrene
Indeno(1,2,3-*cd*)pyrene
Benzo(*ghi*)perylene
Dibenz(*a,h*)anthracene

Figure 2.3 Chemical Structures of Selected PAHs in EPA 610

These 16 PAHs were chosen for study because (i) more information is available than on the others; (ii) they are more harmful than many or most of the others; (iii) there is a greater chance that humans will be exposed to these PAHs than to the others.

2.2 Gasoline Engine

2.2.1 Fundamental Principles of Gasoline Engine Operation

The gasoline engine, the same as a diesel engine, is one type of reciprocating internal combustion engine in which combustion of fuel and air takes place in the cylinder. The combustion is ignited by a spark from the spark plug. This engine is called "spark ignition engine", alternatively.

The spark ignition engine operates on either the four-stroke or the two-stroke cycle. The most commonly used kind for automotive purposes, especially in road vehicles, is the four-stroke spark-ignition engine.

Most internal combustion engines use the reciprocating-piston principle shown in Figure 2.4, wherein a piston slides back and forth in a cylinder and transmits power through, usually, a simple connecting-rod and crank mechanism to the drive shaft. A sequence of operations which is typical of most spark-ignition engines is [8]:

1. An intake stroke to draw a combustible mixture into the cylinder of the engine, Figure 2.4a (intake valve open).

2. A compression stroke to raise the temperature of the mixture, Figure 2.4b (both valves closed).

3. Ignition by spark from spark plug and consequent burning of a homogeneous mixture at the end of the compression stroke, with the

liberation of energy raising the temperature and pressure of the gases; the piston the descends downward on the expansion or power stroke, Figure 2.4c (both valves closed).

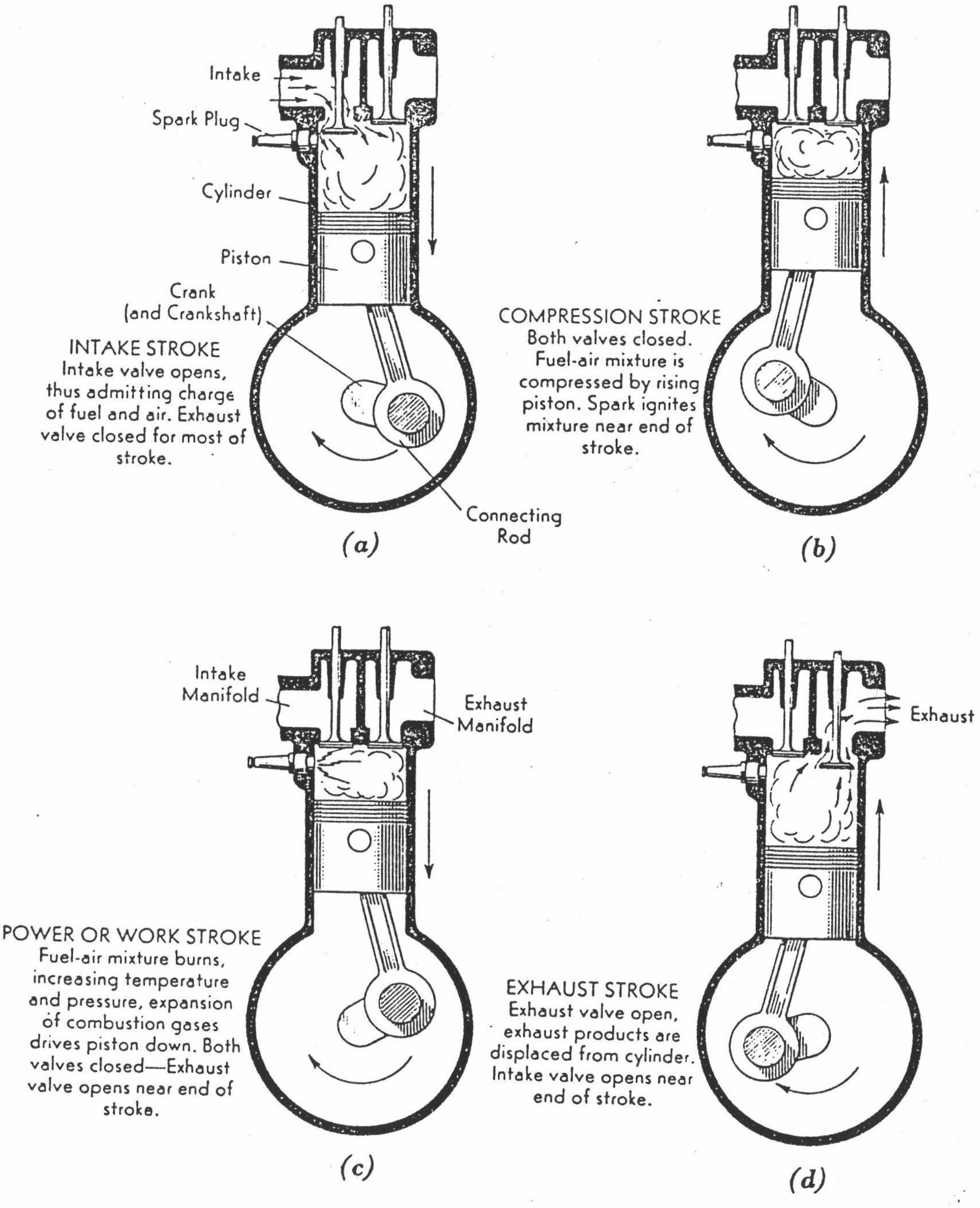


Figure 2.4 The Four-Stroke Spark-Ignition (SI) Cycle [8]

4. An exhaust stroke to sweep the cylinder free of the burned gases. Figure 2.4d (exhaust valve open).

2.2.2 Fuel Metering Systems of Gasoline Engine

There are 2 types of fuel metering systems commonly used in the gasoline engine :

1. Carburetor - The carburetor of the spark-ignition engine meters fuel into the air stream, of the amount dictated by the speed and by the load, in order to form a fairly definite (and homogeneous) mixture of fuel and air which causes effective combustion in the gasoline engine. Figure 2.5 illustrates the basic parts of a simple up-draft carburetor : a venturi, a fuel nozzle with metering orifice, a reservoir of fuel in the float chamber, a throttle, and a choke.

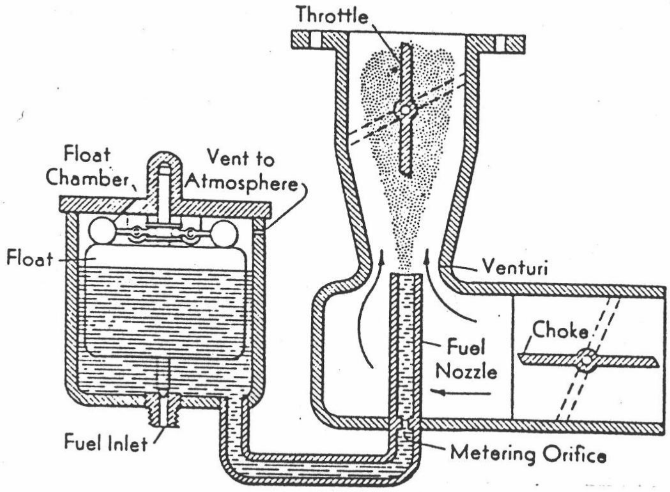


Figure 2.5 Elements of a Simple Updraft Carburetor.

Air, at about atmospheric pressure, is drawn through the venturi when the piston descends on the intake stroke. Because of the smaller diameter at the throat of the venturi, the velocity of the air increases and therefore its pressure decreases. But then the pressure at the tip of the nozzle is less than the pressure (atmospheric) inside the float chamber. Because of this pressure difference, fuel will be sprayed into the air stream, an amount determined by the size of the metering orifice. Note that if the speed of the engine increases, an increased amount of air is drawn through the venturi and therefore a greater pressure drop is created and a proportionately greater amount of fuel is sprayed into the air stream. A carburetor is thus able to maintain approximately a constant ratio between the air and the fuel throughout the speed range of the engine.

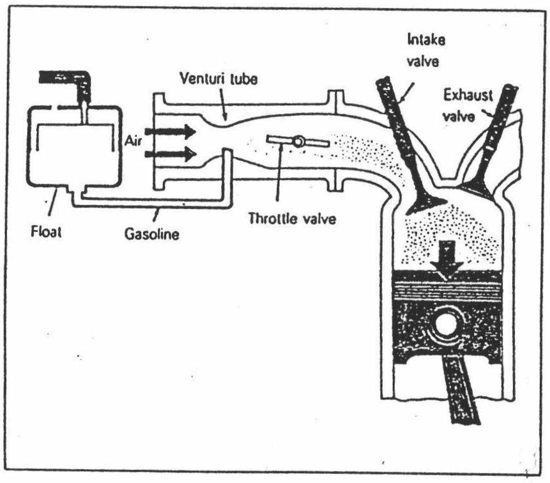


Figure 2.6 Carbureted Gasoline Metering System

2. Electronic Fuel Injector - This fuel injection system, similar to a fuel injector of diesel engine, consists of pumps that have the same shape and operation as diesel pump system. The difference is that the gasoline fuel injector does not inject the fuel into the combustion chamber but the fuel is injected into the intake manifold and the injection pressure is only 4-6 bar. A schematic of an electronic fuel injection system is shown in Figure 2.7.

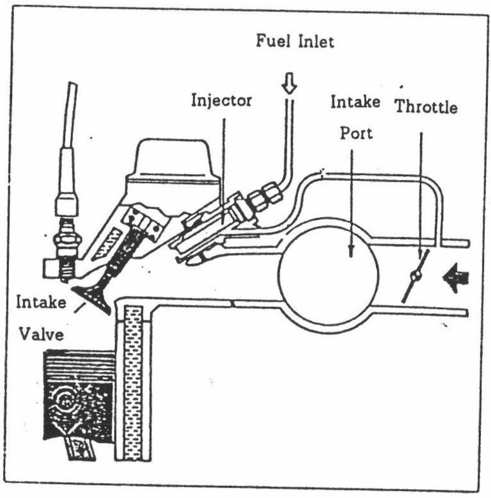


Figure 2.7 Electronic Fuel Injector System of a Gasoline engine

The advantages of electronic fuel injector over the carburetor are :

1. The optimum fuel is charged to the engine in every engine condition. This results in complete combustion, low toxic exhaust, fuel economy, and increased power and torque.

2. Incorporation of a turbocharger is easier because the fuel is injected near an intake valve which need not flow through the compressor before passing to the engine.

3. Faster acceleration, since the fuel is injected close to the cylinder and need not flow through the manifold.

4. Knock is eliminated when an electronic crankshaft sensor and knocking sensor are employed.

2.2.3 Effect of Operating Variables on Gasoline Engine Exhaust Emissions [9]

The exhaust emission of hydrocarbon, carbon monoxide, and oxides of nitrogen can be minimized by the control of several interrelated engine design and operating parameters. These parameters include :

1. *Air-Fuel Ratio (A/F)*

Both CO and HC emissions can be reduced by increasing the air-fuel ratio. Figure 2.8 indicates typical results for CO, HC, and NO_x emissions as a function of *A/F*. Although increasing the *A/F* did reduce the CO and HC, it markedly increased the NO_x emission.

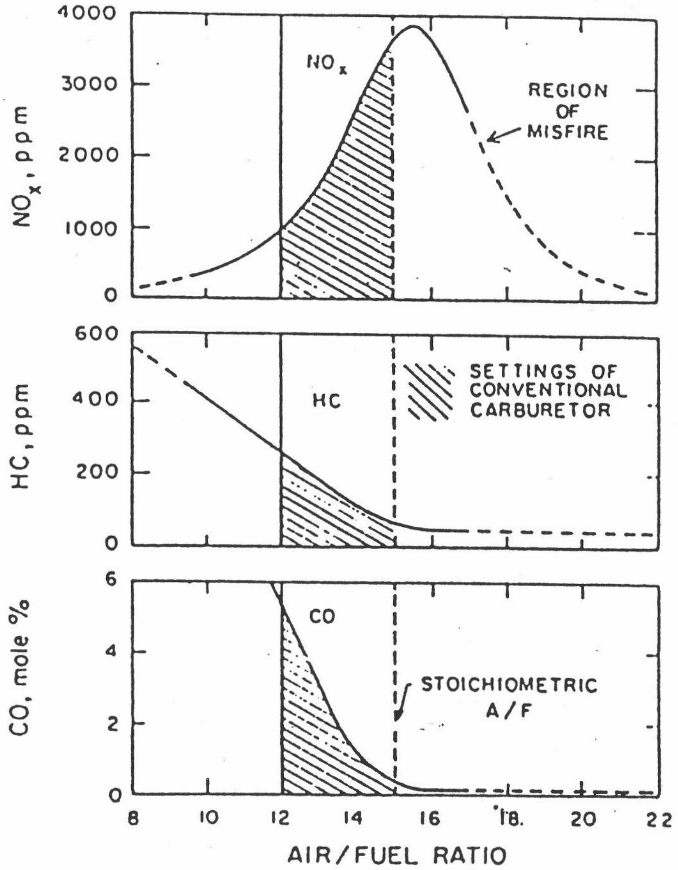


Figure 2.8 Typical Concentration of Unburned Hydrocarbons, CO, and NO_x as a Function of Air-Fuel Ratio at 60 mph

To reduce HC, the cylinder can be redesigned to reduce the crevices (such as between the piston top and combustion chamber) where unburned hydrocarbon could exist. In general the surface to volume ratio of the combustion chamber is an important variable. Large surface areas mean large quench areas and therefore bigger HC emission. The surface to volume ratio can be decreased by reducing the compression ratio or by changing the chamber to a more spherical shape, that is, short and fat.

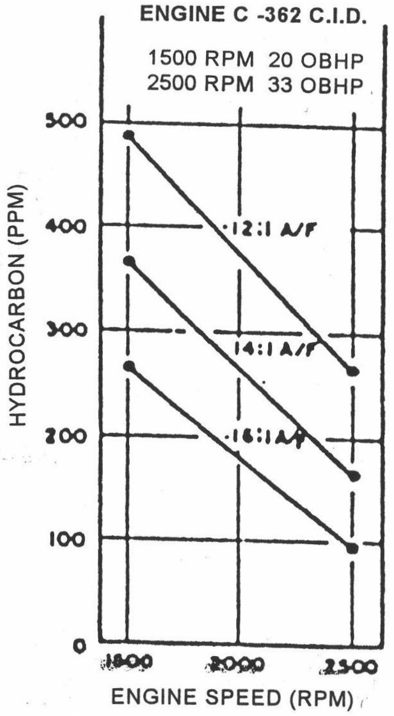


Figure 2.9 Effect of Engine Speed on Exhaust Gas Hydrocarbon Concentration at 12:1, 14:1, and 16:1 Air-Fuel Ratio

2. *Engine Speed*

Emission concentration is markedly reduced at higher engine speeds. Primarily the increase in engine speed improves the combustion process within the cylinder by increasing turbulent mixing and eddy diffusion. This promotes the after-oxidation of the quenched layer. In addition, increased exhaust port turbulence at higher speed promotes exhaust system oxidation reactions through better mixing. Speed has no effect on CO concentration because oxidation of CO in exhaust is kinetically limited rather than mixing limited at the normal exhaust temperature. Figure 2.9 shows the effect of engine speeds on hydrocarbon concentration at 1,500 and 2,000 rpm.

3. *Spark Timing*

The effect of spark timing on HC emission reduction, as shown in Figure 2.10, arises primarily from an increase in exhaust temperature, which promotes CO and HC oxidation, and a decrease in surface to volume ratio during combustion.

In a vehicle the emission reduction achieved by spark retard must be compromised by fuel economy loss considerations. Figure 2.11 shows the effect of spark retarded at 30 mph on fuel economy.

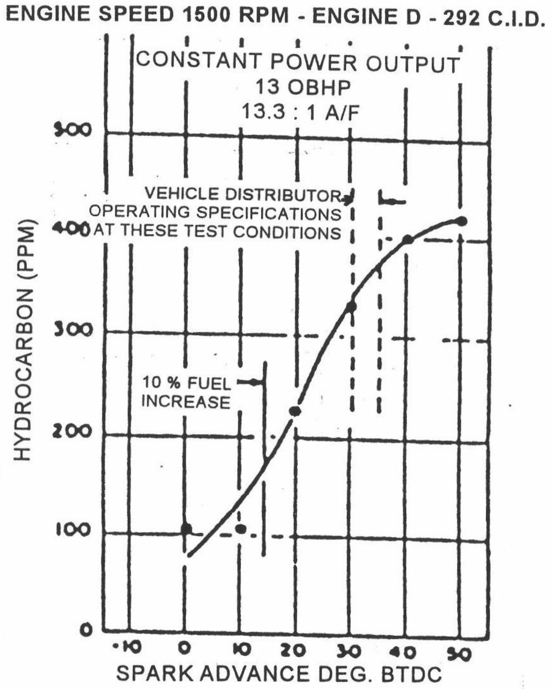


Figure 2.10 Effect of Spark Advance on Exhaust Gas Hydrocarbon Concentrations; Constant Load at Engine Speed of1,500 rpm

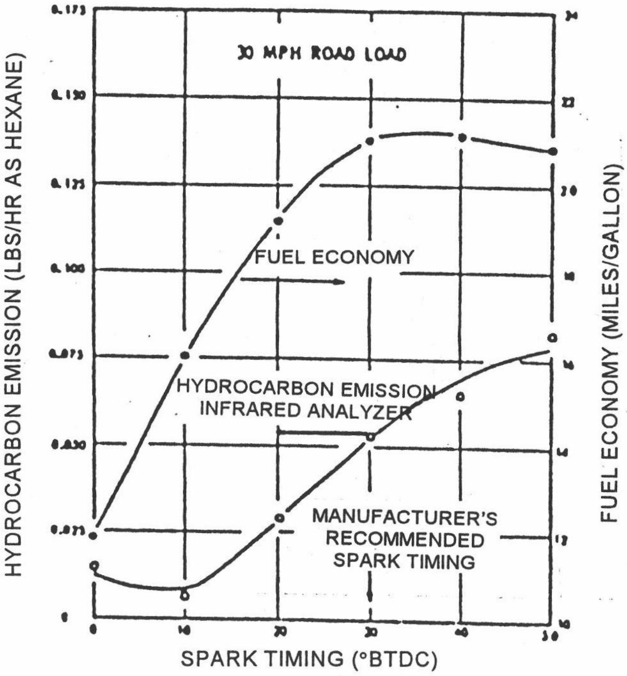


Figure 2.11 Effect of Spark Timing on Exhaust Hydrocarbon Emission and Fuel Economy at 30 mph and Road Load

Spark retard has little effect on CO concentration except at very retarded timing where the lack of time to complete CO oxidation lead to increased CO emissions. Because of the increased air flow required to maintain the power level constant, the mass of CO emitted from the cylinder tends to increase. The increase is offset to some extent by higher exhaust temperatures resulting in improved CO cleanup in the exhaust system. Figure 2.12 shows the CO emission as a function of spark advance.

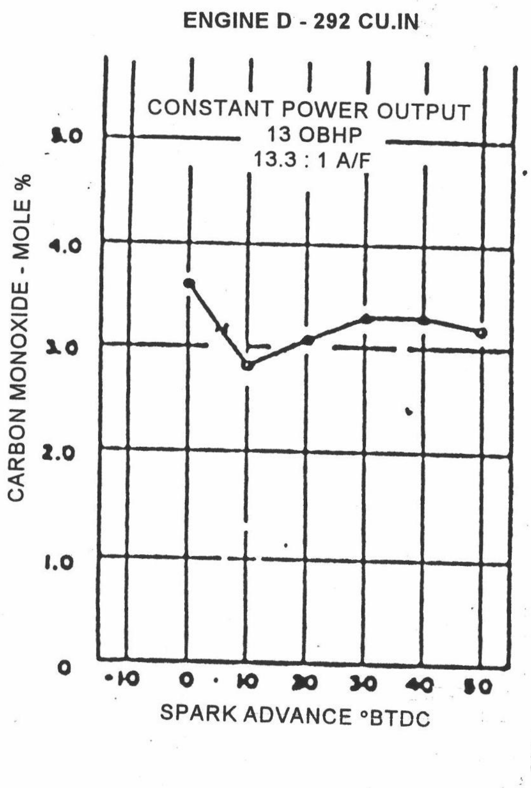


Figure 2.12 Effect of Spark Advance on Exhaust Carbon Monoxide Emission for Fixed Throttle with Constant Load at 1,500 rpm

2.3 Gasoline Fuel

Gasoline is complex liquid mixture of hydrocarbons of 4 basic types : paraffins, olefins, naphthalenes, and aromatics, differing in their properties according to the number and arrangement of carbon and hydrogen atoms in the molecule. Gasoline, having a boiling range of 38-200°C is derived from crude petroleum by refining and contains 5-12 carbon atoms in each molecule.

In the internal combustion engine, gasoline is mixed with air to form a mixture at the appropriate ratio, theoretically, 15 parts by weight of air to 1 part of gasoline, for complete combustion [8]. To satisfy the gasoline engine, the gasoline must meet exacting specifications. Some important performance requirements of gasoline are described as follows :

1. *Antiknock Quality*

To prevent annoying, fuel-wasting, potentially damaging engine knock at all engine speeds and loads, gasoline must have high antiknock quality (octane number). The CFR (Cooperative Fuels Research) engine, a single-cylinder, four-stroke engine in which the compression ratio can be varied at will, has been adopted as the standard for determining octane number, according to ASTM test method. The reference fuels, which are formulated by blending iso-octane (octane number = 100) with n-heptane (octane number = 0), are used for comparing the knock tendency.

There are three types of octane number; (i) Research Octane Number (RON) , obtained by testing with the standard CFR F-1 engine at a low engine speed of 600 rpm and low fuel vapour temperature at 125°F, (ii) Motor Octane Number (MON), obtained by testing with the standard CFR F-2 engine at a high engine speed of 900 rpm and fuel vapour temperature at 300°F, (iii) Road Octane Number, obtained by actual car testing with various speeds and loads, closely corresponding to real driving conditions.

2. *Vapour Pressure*

This property of gasoline indicates whether it will give off enough vapours to start an engine at a given temperature. If the vapour pressure is too high, there is a danger of "vapour lock", in which premature vaporization in fuel line or the fuel pump partially or completely stops the flow of liquid fuel.

3. *Distillation Characteristics*

For fast warmup, smooth acceleration, and proper distribution of the fuel among an engine's cylinders, the gasoline must vaporize increasingly as carburetor and manifold temperatures rise.

In addition to the properties of gasoline itself, additives are invariably required for many purposes.

1. Antiknock - To reduce or eliminate the knock in the engine and increase the combustion efficiency.

2. Antioxidants - To inhibit the oxidation reaction which forms gums and thereby tend to improve the stability of gasoline in use or in storage.

3. Corrosion and Rust inhibitor - To prevent rust and corrosion in storage tank, line, and the fuel system of engine arising from the small amount of water usually present in gasoline.

4. Metal deactivator - To destroy the activity of traces metal, particularly copper, that calalyze the oxidation of hydrocarbons in gasoline to form gum.

5. Demulsifier - To remove water from gasoline faster.

6. Detergent/Dispersant - To prevent deposits in carburetors and manifold, and romove the deposits already formed so that the engine can run smoothly.

7. Combustion deposit modifier - To alter the chemical character of combustion chamber deposits and so reduce surface ignition and spark plug fouling.

8. Valve seat recession protection - To protect the valve seat recession of the exhaust valve, which is a soft metal, from corrosion when using the unleaded gasoline by lubricating it.

9. Dye - To identify various makes or grades of gasoline.

2.4 Dispersant Gasoline Additive [4]

Dispersants are non-metallic or ashless cleansing agents. The structure of ashless dispersants is similar to the structure of a detergent in that the dispersant has a hydrocarbon tail or oleophilic group which enables the dispersant to be fully soluble in the base fuel used. The dispersant also has a polar head. The polarity of a dispersant is derived from the inclusion of oxygen, phosphorus, or nitrogen atoms into the molecule. Figure 2.13 shows the stylized structure of an ashless dispersant.

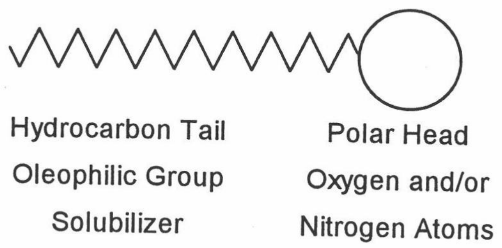
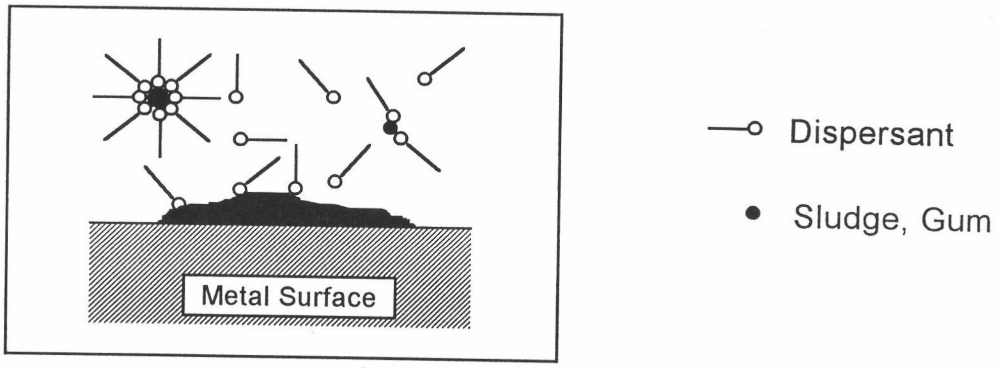


Figure 2.13 Stylized Dispersant [4]

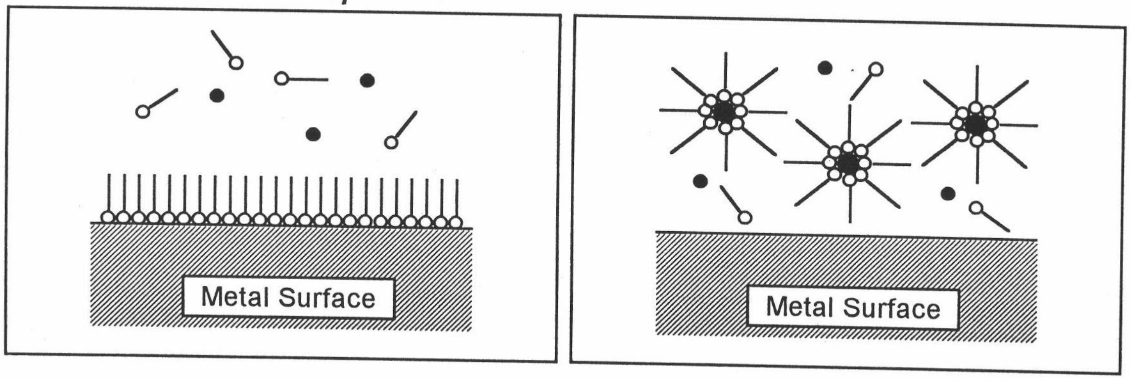
Most dispersants currently in use are prepared from polyisobutylenes of 1,000 to 10,000 molecular weight. Their polar functionality arises from amino and/or hydroxyl (alcohol) groups. The connecting groups, in most cases, are either phenols or succinic acids. The products with succinic acid groups are called alkenyl succinimides and succinate esters. The products from phenols are alkyl hydroxybenzyl poly amines (also called Mannich dispersants because of the name of the German chemist who discovered the method of preparation).

The dispersants are used in gasoline fuel to provide fuel inject, caburetor, and valve cleanliness. Engine life is prolonged and undesirable engine exhaust emissions are reduced. The terms "detergents" and "dispersants" are often used interchangeably because both additive types keep insoluble combustion debris and fuel oxidation products dispersed with the fuel. Detergents are normally utilized to minimize high-temperature engine varnish and lacquer deposits while dispersants are used to control low-temperature engine sludge deposits. In addition to the cleansing action, the dispersants have the ability to disperse particulate mater in an extremely fine and harmless state and hold it in suspension. In this way it will pass through the fuel system into the combustion chamber and burn with the fuel [10]. The harmful products of combustion and other contaminants are rendered harmless by the polar ends of dispersants. The hydrocarbon chain of dispersants helps to solubilize or suspend the debris.

The mechanism of the dispersant interaction with sludge is shown in Figure 2.14. The polar groups in the dispersant preferentially attach themselves to metal surface and to any particulates present since these also have a polar nature. The non-polar part of the molecule sticks out into the fuel hydrocarbons so that a monomolecular film is formed on the surfaces, preventing deposition and particle aggregation. Particles are thus carried on into the combustion chamber and burnt. Deposits that have already been laid down can gradually be removed by this mechanism, which, in effect, solubilizes them.



Clean Up



Keep Clean

Figure 2.14 Sludge Dispersion

Chemically, polymeric dispersants are relatively high molecular weight materials and can be divided into three chemical groups - succinimides, polybutene amines and polyether amines (Figure 2.15) [10]. The concentration of polymeric dispersants added to fuel is 20-600 ppm.

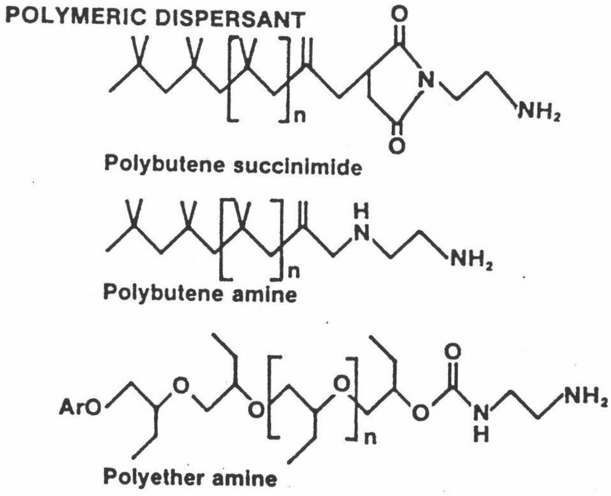


Figure 2.15 Polymeric Dispersant Gasoline Additives

2.5 PAHs in Exhaust Emission

Two major pathways are recognized as sources of PAH recovered in the exhaust emissions : (i) survival of PAHs from the fuel; (ii) combustion reactions in which fragments of fuel or lube oil are pyrosynthesized to produce the PAHs. In (i) the carbon skeleton of the PAHs remain unchanged, while in (ii) it is newly formed in the combustion chamber. The emission rates of PAHs by an internal combustion engine are related to a number of factors such as composition of both fuel and lubricating oil, mileage of engine, number of revolutions per minute (rpm), change of speed, and load under which the engine is running [11].

Due to their low vapour pressures, most PAHs will immediately condense and form a thin film (adsorb) onto soot particles or form as very small paricles themselves [12]. However, the dominant amount of the low molecular weight PAHs was found in the vapour phase [13].

2.5.1 Exhaust Sampling Systems

There are two standard methods in exhaust sampling for determination of PAHs in exhaust emission : the U.S. EPA dilution tunnel and filtering system, and the total exhaust solvent scrubbing apparatus (TESSA).

1. *The Dilution Tunnel* [14]

This method was devised to mimic the natural dilution and cooling of exhaust as it leaves the tailpipe. The schematic of exhaust gas dilution tunnel is shown in Figure 2.16. After combustion in the engine, particulate carbon scavenges organic components from the vapour phase. These include the PAHs which may originate from unburned fuel and lubricating oil or from pyrosynthetic reactions involving the incomplete combustion of fuel. The PAHs adsorbed onto particulate carbon are sampled by a filter and may be extracted, usually using Soxhlet extraction, into solvents to produce a soluble organic fraction (SOF), however, the filter will not efficiently sample those hydrocarbons and PAHs which have remained in the vapour phase.

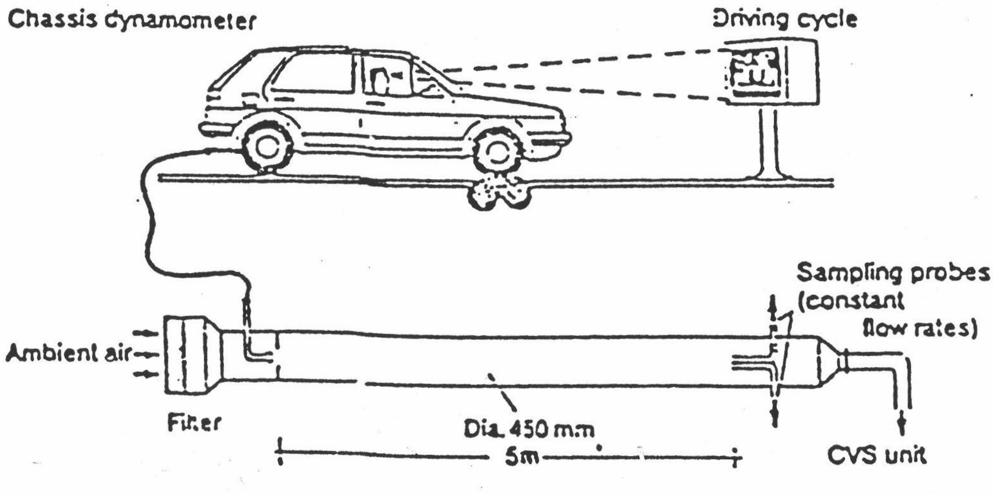
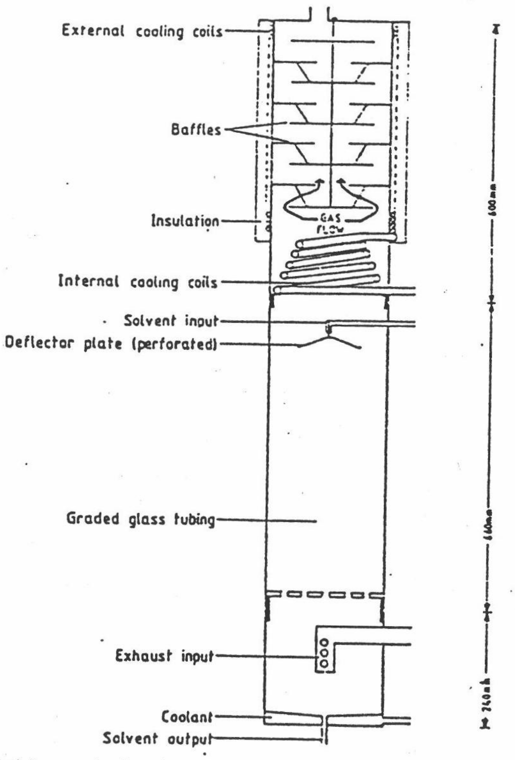


Figure 2.16 Schematic of Exhaust Gas Dilution Tunnel

The filter method suffers from the disadvantage that artifacts may be formed on the carbon particles as the diluted exhaust continues to pass through the filter.

2. *The Total Exhaust Solvent Scrubbing Apparatus (TESSA)* [15]

The TESSA system consists of a verticle stainless steel tower (~1.5x0.3 m) connected by a short (50 cm) heated transfer line to the engine. The tower comprises two sections. Collection of the exhaust organics occurs in the lower section, which is filled with graded-glass tubing to maximize the area of contact between solvent and exhaust gases. The upper section is used to cool the exhaust effluent and contains a series of cooling baffles. The exhaust is sampled using a pressure-controlled countercurrent flow of solvent (dichloromethane-methanol 1:1) which strips the organic species from the exhaust gases as they enter the apparatus. The exhaust sample is collected in large flask at the base of the tower. Figure 2.17 shows the schematic of the total exhaust solvent scrubbing apparatus.



Stainless-steel exhaust scrubbing tower.

Figure 2.17 Schematic of the Total Exhaust Solvent Scrubbing Apparatus (TESSA)

In addition to the both systems, filtration and condensation-filtration systems were employed in many studies [16,17,18]. Glass fibre filter has been used for trapping particulate matter formed in the exhaust and polyurethane foam has been used for trapping the semivolatile phase. The particulate and semivolatile samples were then subjected to the extraction, usually using Soxhlet extraction, and separation procedures. The most commonly used solvents for the extraction of PAHs from particulates are dichloromethane, cyclohexane and mixtures of benzene with an alcohol [18].

2.5.2 Analytical Methods

Because of the environmental concerns over PAHs, a wide variety of analytical methods have been used, with various sample extraction, cleanup, and concentration procedures. Analysis is commonly either by capillary GC with FID or MS detection, or by HPLC with detection by UV diode array and fluorescence [19]. Gas chromatography has been widely applied to the analysis of PAHs. High-efficiency separation and resolution can be obtained by using capillary GC column.

Mass spectrometry, alone or in combination with GC, has been used for the separation, quantitation and identification of PAHs in environmental samples. Since PAHs have aromatic structures, mass spectra are characteristic and present an intense peak cluster in the region of the molecular ion under electron impact ionization conditions, so that mass spectrometric interferences may not play an important role in their determination.

The problem of chromatogram complexity can be solved either by using specific detectors, such as the Electron Capture Detector (ECD), when this is possible, or by using a selective program in the Selected Ion Monitoring (SIM) detection of the GC effluent [20]. The use of single or multiple ion monitoring may result in picogram level detection limits for particular compounds [19].

2.6 Literature Review

Accumulated evidence indicates that PAHs are present in automotive-engine exhausts. This source contributes significantly to urban atmospheric pollution in terms of known or potential carcinogenic factors such as some of the polynuclear compounds. Haffman and Wynder (quoted in [21]) have identified over 20 different PAHs in the "tars" collected from the exhaust of spark-ignition engines, and a number of these compounds are known carcinogens. They reported that the carcinogenic activity of these exhaust "tars" on mouse skin was in the range of 1-25th to 1/50th of that of the same concentration of PAH carcinogens in cigarette smoke.

Much of the early research associated with the emission of PAHs from gasoline engines was carried out as a collaborative effort between the General Motors Research Laboratories and the Sloan-Kettering Institute for Cancer Research (quoted in [21]). Mckee and McMahon reviewed the early work associated with PAHs in vehicles emission.

Begeman and Colucci measured BaP in the exhaust of a gasoline-powered engine operating on a driving cycle which simulated city driving and reported that under their test conditions approximately 36% of the BaP in the engine exhaust could be directly attributed to the BaP initially in the fuel. Between 0.1 and 0.2% of the BaP in the fuel was reported to survive the combustion process and was recovered from the exhaust, 5% of the BaP was accumulated in the crankcase oil, and some of the original BaP was reported to be converted into other PAHs and more polar compounds (quoted in [21]).

In a subsequent, more comprehensive article, Begeman and Colucci studied the influence of *A/F* ratio, driving mode, oil consumption, and fuel compositon on the PAHs emitted by spark-ignition engines. During the course of the studies, the contribution of PAHs in gasoline to PAH emissions, the effects of two emission control systems designed to reduce carbon monoxide and hydrocarbons in exhaust PAHs emissions, and the average emission of PAHs from a twenty-five car sample of privately owned vehicles in simulated city driving were determined. The results clearly indicate that the concentrations of both benz(*a*)anthracene (BaA) and BaP are significantly greater in the deceleration mode than in any of the other operating modes. However, on the basis of total mass emissions, the PAHs emissions were highest during accelerations when large total mass flow rates were encountered. Based on these results, it can be concluded that the operation of the engine in transient modes contributes significantly to total PAHs emissions during a typical city driving cycle. The effects of *A/F* ratio on PAHs emission were also studied and it was found that both BaP and BaA emissions were considerably higher for rich carburetion than for either stoichiometric or lean carburetion. These results relating high PAHs emissions to transient engine operation and rich carburetion are in general agreement with the work of previous investigators (quoted in [21]).

High oil consumption in the test engines lead to a significantly increase PAHs emission. In one series of tests with the 283-in^3 displacement engine operating on regular fuel in a simulated city driving cycle, the effect of oil consumption on PAHs was evaluated by systematically increasing the oil consumption in a “normal” engine by removal of intake valve guide seals, exhaust seals, or the expansion rings under one or more of the piston oil control rings. From the results, it can be concluded that the BaP emissions are approximately proportional to oil consumption when most of the oil is introduced into the chamber past the piston rings. Oil consumption due to leakage into the exhaust system along the exhaust valve stems also follows this trend. However, the BaP emissions were not significantly increased when the increased oil consumption was due to unsealed intake valve guides.

Analysis of samples of crankcase oil obtained from the test engines indicated surprisingly high concentration of PAHs. Based on these measurements it was reported that, when operating the engine under normal oil consumption conditions, the rate of entry of BaP into the crankcase was approximately 10 times greater than the rate of emission of BaP in the exhaust gas. Based on these findings, the authors concluded that most of the BaP which enters the crankcase is formed in the combustion chamber by either pyrolysis of the fuel or oil, or is absorbed by the oil film left on the cylinder wall and is subsequently scraped into the crankcase.

Three different fuels with different initial concentrations of BaP were tested in order to ascertain if the correspondence between PAHs in the exhaust could be directly related to the quality of BaP in the fuel as quoted in [21]. The PAHs emissions were reported to be directly related to PAHs in the gasoline, but other unidentified fuel consumption factors also seemed to contribute these emissions. A series of tests also indicated that two emission control systems, designed to reduce carbon monoxide and volatile hydrocarbons in the exhaust gases, were also effective in reducing the BaP emissions by factors ranging from 3 to 27 when compared to emissions from the same uncontrolled engines.

Twenty-five cars were tested by Begeman and Colucci (quoted in [21]) in order to determine if, on the average, older cars emitted more PAHs than newer cars. In all cases the older group of cars was found to emit significantly more PAHs than the newer group. The PAHs emissions from the various cars differed widely due to the large variance of *A/F* ratios, oil economies, and possible fuel composition. However, the authors proposed that the higher average emission recorded by the older group of cars is most probably due to the higher oil consumption rate of this group of cars. Hangebrauch *et al.* had reported the same results [21].

Valori et al. (quoted in [11]) identified and determined several PAHs both in the gasoline engine and in the liquefied petroleum gas engine exhausts. A combined condensation-filtration apparatus was constructed for sampling of the exhausts. In the gasoline engine exhausts, 19 PAHs were identified and determined.

Alsberg et al. (quoted in [22]) investigated gasoline exhaust particulate extracts chemically and biologically. The results showed that the crude particle extracts gave a response in all test systems and also indicated a metabolism-dependent effect, characteristic for PAH.

Westerholm *et al.* [23] characterized, chemically and by mutagenicity tests, exhaust emissions from a fuel-injected, Otto engine equipped car driven according to the U.S. Federal Test Procedure (FTP-73). Four fuel qualities of different PAH content were used. From the results obtained concerning fuel-dependent exhaust emissions, it could be concluded that a linear relationship existed between input through fuel and output through the exhaust emission for certain individual PAH.

Mi *et al.* [23] investigated the PAH emission from a gasoline-powered engine operated on a dynamometer. A 95-leadfree gasoline and a premium leaded gasoline were used as fuels. The engine was simulated for the idling condition and for the cruising speeds at 40, 80, and 110 km/hr. The results showed that the fuel combustion could be a generation process for 11 PAHs.

Khalili *et al.* [25] evaluated the chemical composition of the major sources of PAHs in the Chicago metropolitan area. GC/FID and

GC/MS techniques were used to analyze the samples. The sources sampled were coke ovens, highway vehicles, heavy-duty diesel engines, gasoline engines and wood combustion. Results of this study showed that 2- and 3-ring PAHs were resposible for 98, 76, 92, 73, and 80% of the total concentration of measured 20 PAHs for coke ovens, diesel engines, highway tunnels, gasoline engines, and wood combustion samples, respectively. 6-ring PAHs such as indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene were mostly below the detection limit of this study and only detected in the highway tunnel, diesel and gasoline engine samples.

In 1990, Schuermann *et al.* from Volkswagen AG, Germany [26] investigated the emission on unregulated motor vehicle exhaust gas components carried out at VW on 18 VW/Audi passenger cars of model years 1978 to 1986. The unregulated exhaust gas components consisted of 21 compounds and classes of compounds which include PAHs. The emission testing was conducted on a chassis dynamometer according to three different test procedures. These tests are the US-75-Test, the Sulfate-Emission-Test, and the Highway-Driving-Test. PAHs in the exhaust gas of gasoline and diesel engines were sampled by the total flow method using filtration along with adsorption, and analyzed by TLC, HPLC, GC/FID, and GC/MS. 11 PAHs were selected for investigation in this study. A particularly noticeable feature is that the emission results of the gasoline engine vehicles with catalysts are at least one order of magnitude smaller than those of the two other vehicle groups (gasoline engine vehicles without catalysts or diesel engine vehicles).

In 1994, Adibis, from its Copenhagen office [18], contracted Motortestcenter to perform a test program according to the guidelines of the Swedish EPA on one detergent additive and one valve seat protection additive in gasoline fuel. The test included CO, HC, NO_x, and particulate emissions as well as PAH, mutagenic activity and TCDD receptor activity. Sampling of exhausts were performed on diluted exhausts after dilution tunnel and with the Constant Volume Sampler (CVS) equipped with a 6 m^3/min venturi. The analyses of PAH were performed on particulates and in the semivolatile phase. Sampling was performed on glass-fibre filter and in a following polyurethane foam plug. The extracts of samples were separated on a capillary gas chromatography column. Analysis was performed using mass fragmentography. The results showed no difference with additives.